

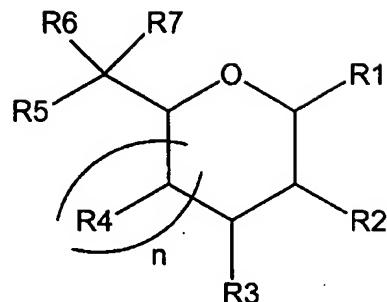
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DT04 Rec'd PCT/PTO 28 SEP 2004

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Claims:

1. A compound of formula I



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formula I

Wherein,

n is 0 or 1;

R1 is selected from the group consisting of hydrogen or -

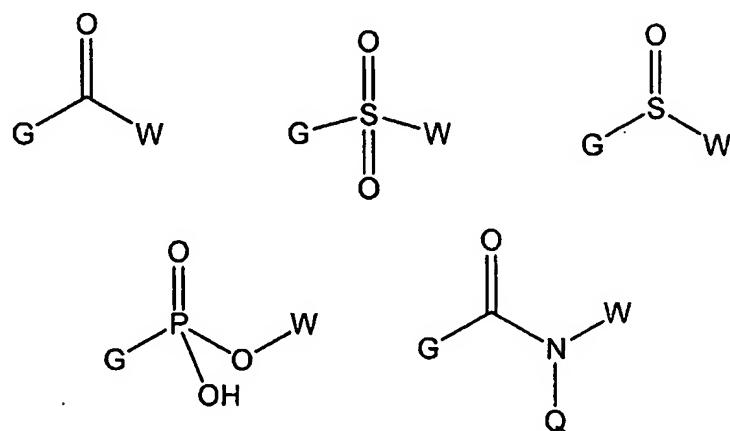
10 N(Z)Y wherein;

When R1 is -N(Z)Y, then:

R6 and R7 are hydrogen;

Y is selected from hydrogen, or the following, where G denotes the

15 point of connection to the nitrogen atom in N(Y)Z;



Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

The groups W are independently selected from the group consisting of substituted or unsubstituted alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

5        The groups X1 are independently selected from the group consisting of substituted or unsubstituted alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

at least one of the groups R2, R3, R4 and R5 is selected from the  
10      group consisting of -OX2 or -N(T)Y, and the others of the groups R2, R3, R4 and R5 are independently selected from hydrogen, -OH, -OX2, -N(T)Y, wherein Y is as defined above, T is selected from hydrogen or X2; and X2 is independently selected from substituted or unsubstituted alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl or heteroarylalkyl of 1 to 20  
15      atoms,

With the provisos that:

- a. X2 may not be another carbohydrate ring, a cyclitol ring or contain another carbohydrate ring,
- 20      b. all of the X2 substituents may not be the same;

When R1 is H,

R6 and R7 are hydrogen, or together form a carbonyl oxygen;

25      at least two of the groups R2, R3, R4 and R5 are selected from the group consisting of -OX2 or -N(T)Y, and the others are independently selected from hydrogen, -OH, -OX2, -N(T)Y, wherein Y is as defined above, T is selected from hydrogen or X2; and X2 is independently selected from substituted or unsubstituted alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl or  
30      heteroarylalkyl of 1 to 20 atoms,

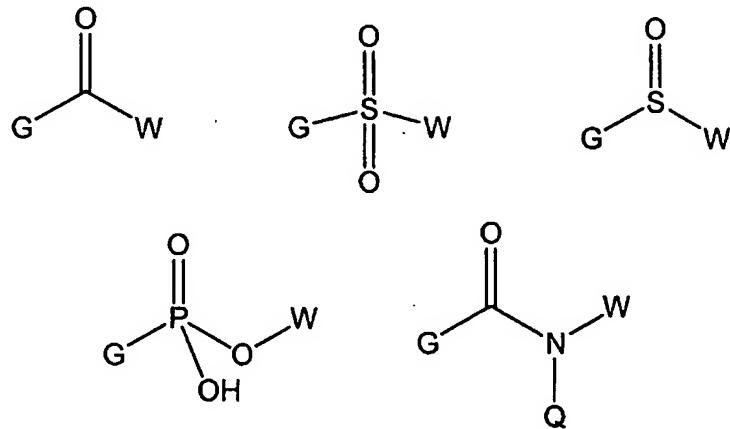
With the provisos that:

- c. X2 may not be another carbohydrate ring, a cyclitol ring or contain another carbohydrate ring,
  - d. all of the X2 substituents may not be the same.
- 5     2.     The compound of claim 1, wherein wherein the ring is selected from the pyran or furan form and the anomeric center is selected from the  $\alpha$  or  $\beta$  configuration.
- 10    3.     The compound of claim 1, wherein the groups Z and Y are combined to form a monocyclic or bicyclic ring structure of 4 to 10 atoms.
- ( )
4.     The compound of claim 3, wherein the ring structure is further substituted with X1 groups.
- 15    5.     The compound of claim 1 in wherein W is substituted with a moiety selected from the group consisting of OH, NO, NO<sub>2</sub>, NH<sub>2</sub>, N<sub>3</sub>, halogen, CF<sub>3</sub>, CHF<sub>2</sub>, CH<sub>2</sub>F, nitrile, alkoxy, aryloxy, amidine, guanidiniums, carboxylic acid, carboxylic acid ester, carboxylic acid amide, aryl, cycloalkyl, heteroalkyl, heteroaryl, aminoalkyl, aminodialkyl, aminotrialkyl, aminoacyl, carbonyl, 20    substituted or unsubstituted imine, sulfate, sulfonamide, phosphate, phosphoramide, hydrazide, hydroxamate, hydroxamic acid.
- ( )
6.     The compound of claim 1 in wherein X1 is substituted with a moiety selected from the group consisting of OH, NO, NO<sub>2</sub>, NH<sub>2</sub>, N<sub>3</sub>, halogen, CF<sub>3</sub>, CHF<sub>2</sub>, CH<sub>2</sub>F, nitrile, alkoxy, aryloxy, amidine, guanidiniums, carboxylic acid, carboxylic acid ester, carboxylic acid amide, aryl, cycloalkyl, heteroalkyl, heteroaryl, aminoalkyl, aminodialkyl, aminotrialkyl, aminoacyl, carbonyl, substituted or unsubstituted imine, sulfate, sulfonamide, phosphate, phosphoramide, hydrazide, hydroxamate and hydroxamic acid.
- 25    7.     The compound of claim 1, wherein Y is hydrogen.
- 30

8. The compound of claim 1 in wherein X2 is substituted with a moiety selected from the group consisting of OH, NO, NO<sub>2</sub>, NH<sub>2</sub>, N<sub>3</sub>, halogen, CF<sub>3</sub>, CHF<sub>2</sub>, CH<sub>2</sub>F, nitrile, alkoxy, aryloxy, amidine, guanidiniums, carboxylic acid, carboxylic acid ester, carboxylic acid amide, aryl, cycloalkyl, heteroalkyl,  
5 heteroaryl, aminoalkyl, aminodialkyl, aminotrialkyl, aminoacyl, carbonyl, substituted or unsubstituted imine, sulfate, sulfonamide, phosphate, phosphoramide, hydrazide, hydroxamate and hydroxamic acid.
9. The compound of claim 1 wherein at least three of the groups R2, R3,  
10 R4 and R5 are selected from -OX2 or -N(T)Y;
10. The compound of claim 1 wherein R1 is hydrogen.
11. The compound of claim 10 wherein independently at least one of R2,  
15 R3, R4, or R6 is -N(T)Y, and at least one is -OX2.
12. The compound of claim 10 wherein independently at least two of R2,  
R3, R4, or R6 are -OX2.
- 20 13. The compound of claim 10 wherein at least two of R2, R3, R4, or R6  
is -N(T)Y.
14. The compound of claim 1 wherein R1 is -N(Z)Y.
- 25 15. The compound of claim 14 wherein at least one of R2, R3, R4, or R6  
is -N(T)Y.
16. The compound of claim 14 wherein at least two of R2, R3, R4, or R6  
is -N(T)Y.
- 30 17. The compound of claim 14 wherein at least two of R2, R3, R4, or R6  
are -OX2.

18. A method of synthesis of compounds of claim 10, wherein n is 1, comprising the step of reducing a synthetic intermediate of formula III, in which
- 5 V is bromine or chlorine,  
R6 and R7 are hydrogen, or together form a carbonyl oxygen,  
R5, R4, R3, and R2 are selected from the group consisting of OH, O-acyl, N<sub>3</sub>, NHDde, NHDTMP, NHZ, NHBOC, phthalimide, OX2, N(T)Y and an O-protecting group,
- 10 X2 is independently selected from alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl or heteroarylalkyl of 1 to 20 atoms,  
T is hydrogen or X2,  
Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(T)Y;

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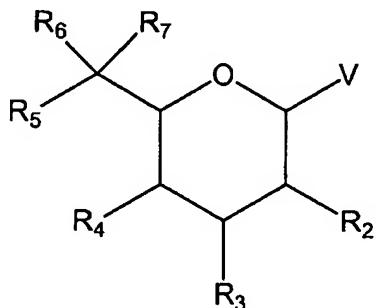
Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

20 The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

The groups X1 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

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general formula III

19. The method of claim 18, wherein R<sub>6</sub> and R<sub>7</sub> together form a carbonyl oxygen and R<sub>5</sub> is O-alkyl, O-arylalkyl or O-aryl.

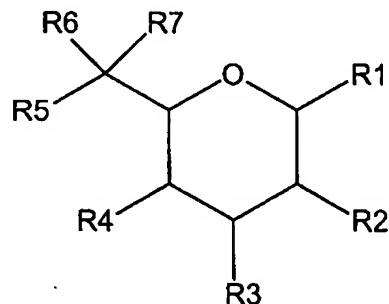
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20. The method of claim 19, wherein the R<sub>5</sub> substituent is substituted with a moiety selected from the group consisting of OH, NO, NO<sub>2</sub>, NH<sub>2</sub>, N<sub>3</sub>, halogen, CF<sub>3</sub>, CHF<sub>2</sub>, CH<sub>2</sub>F, nitrile, alkoxy, aryloxy, amidine, guanidinium, carboxylic acid, carboxylic acid ester, carboxylic acid amide, aryl, cycloalkyl, heteroalkyl, heteroaryl, aminoalkyl, aminodialkyl, aminotrialkyl, aminoacyl, carbonyl, substituted or unsubstituted imine, sulfate, sulfonamide, phosphate, phosphoramide, hydrazide, hydroxamate, hydroxamic acid.

21. The method of claim 18, wherein the O- protecting groups comprise acetals and ketals which protect two adjacent oxygens.

22. A method of synthesis of compounds according to claim 14, in which n is 1, comprising the step of reacting a compound of formula III with an azide nucleophile, to form an anomeric azide and reduction of the anomeric azide to form an anomeric amine and reaction of the anomeric amine with an 5 electrophile.

23. A method of combinatorial synthesis of compounds of claim 1, wherein n is 1, comprising the step of immobilizing a compound of formula IV onto a support.



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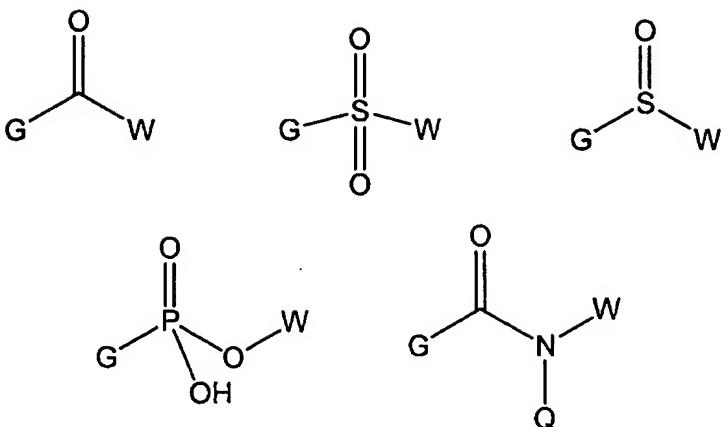
general formula IV

wherein

15 R6 and R7 are hydrogen, or together form a carbonyl oxygen;  
R1 is selected from the group consisting of hydrogen; -N(Z)Y and -C(Z)Y  
wherein;

When R1 is -N(Z)Y, then:

Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(Y)Z;



Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

- 5 The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

- 10 The groups X1 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

When R1 is  $-C(Z)Y$ , then:

- 15 Y is selected from the group consisting of two hydrogen atoms, a double bonded oxygen (=O) to form a carbonyl, and a triple bonded nitrogen to form a nitrile,

Z is absent, or is selected from hydrogen or U,

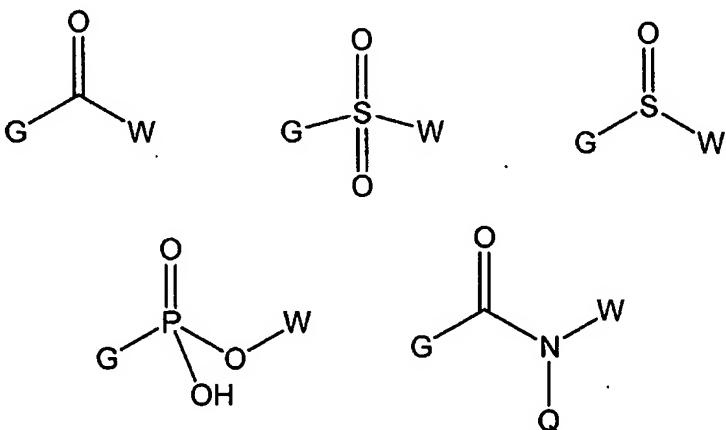
- Wherein U is selected from the group consisting of alkyl, alkenyl, 20 alkynyl, heteroalkyl, aminoalkyl, aminoaryl, aryloxy, alkoxy, heteroaryloxy, aminoaryl, aminoheteroaryl, thioalkyl, thioaryl or thioheteroaryl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

R5, R4, R3, and R2 are selected from the group consisting of OH, O-acyl, N<sub>3</sub>, NHDde, NHDTMP, NHZ, NHBOC, phthalimide, OX2, N(T)Y and an O-protecting group, and the linkage between the compound of formula IV and the support is through any one of positions R1, R2, R3, R4 or R5,

- 5 X2 is independently selected from alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl or heteroarylalkyl of 1 to 20 atoms,  
T is hydrogen or X2,

Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(Y)Z;

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Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

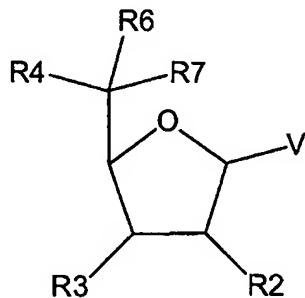
- 15 The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

- The groups X1 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacetyl, heteroarylacetyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

24. The method of claim 23 wherein the support is selected from the group consisting of derivatised polystyrene, tentagel, wang resin, MBHA resin, aminomethylpolystyrene, rink amide resin DOX-mpeg, and polyethylene glycol.

5

25. A method of synthesis of compounds according to claim 13, in which n is 0, comprising the step of reacting a compound of formula V in the presence of a lewis acid with an azide source to form an anomeric azide, reduction of the anomeric azide to form an anomeric amine and reaction of 10 the anomeric amine with an electrophile.



general formula V

in which V is -OAcyl,

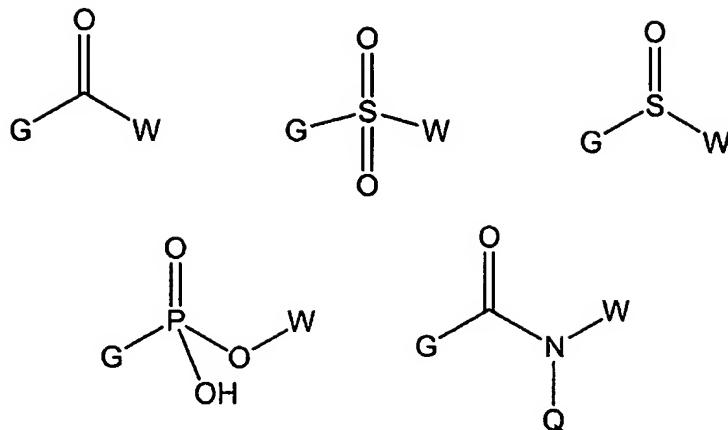
15 R6 and R7 are hydrogen, or together form a carbonyl oxygen,  
R4, R3, and R2 are selected from the group consisting of OH, O-acyl, N<sub>3</sub>,  
NHDde, NHDTMP, NHZ, NHBOC, phthalimide, OX2, N(T)Y and O-protecting  
group,

X2 is independently selected from alkyl, alkenyl, alkynyl, heteroalkyl, aryl,  
20 heteroaryl, arylalkyl or heteroarylalkyl of 1 to 20 atoms,

T is hydrogen or X2,

Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(Y)Z;

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Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

5        The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

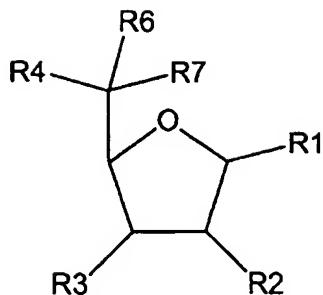
            The groups X1 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl,

10      heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

26.      The method of claim 25, wherein R6 and R7 together form a carbonyl oxygen, and R4 is substituted O-alkyl, O-arylalkyl or O-aryl.

15      27.      A method of combinatorial synthesis of compounds of claim 1, wherein n is 0, comprising the step of immobilizing a compound of formula VI onto a support,

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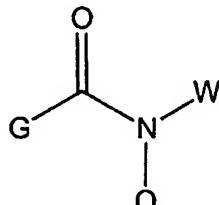
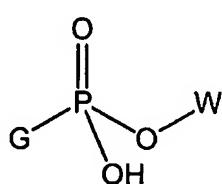
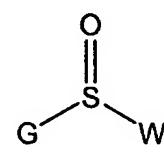
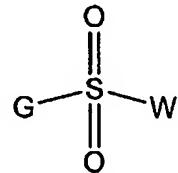
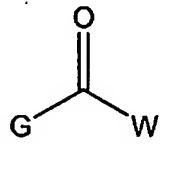


general formula VI

Wherein R1 is selected from the group consisting of hydrogen; -N(Z)Y and -C(Z)Y wherein;

- 5 When R1 is -N(Z)Y, then:

Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(Y)Z;



10

Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

- 15 heteroarylalkyl of 1 to 20 atoms,

The groups X1 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

- 5 When  $R_1$  is  $-C(Z)Y$ , then:

Y is selected from the group consisting of two hydrogen atoms, a double bonded oxygen (=O) to form a carbonyl, and a triple bonded nitrogen to form a nitrile,

- 10 Z is absent, or is selected from hydrogen or U,

Wherein U is selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aminoalkyl, aminoaryl, aryloxy, alkoxy, heteroaryloxy, aminoaryl, aminoheteroaryl, thioalkyl, thioaryl or thioheteroaryl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms.

- 15

R6 and R7 are hydrogen, or together form a carbonyl oxygen.

R4, R3, and R2 are selected from the group consisting of OH, O-acyl, N<sub>3</sub>.

NHDde, NHDTMP, NHZ, NHBOC, phthalimide, OX2, N(T)Y and O-protecting group.

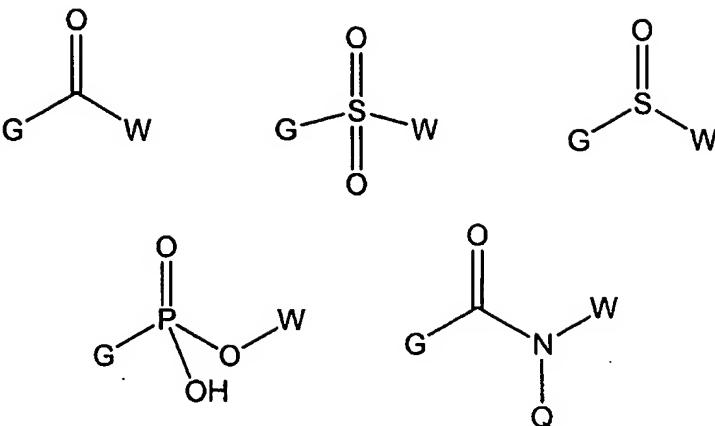
- 20 X2 is independently selected from alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl or heteroarylalkyl of 1 to 20 atoms

T is hydrogen or X?

Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(Y)Z:

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Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

5 The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms ,

The groups X1 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl,

10 heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

and the linkage between the compound of formula VI and the support is through any one of positions R1, R2, R3, or R4.

28. The method of claim 27, wherein the support is selected from the  
15 group consisting of derivatised polystyrene, tentagel, wang resin, MBHA resin, aminomethylpolystyrene, rink amide resin DOX-mpeg, and polyethylene glycol.

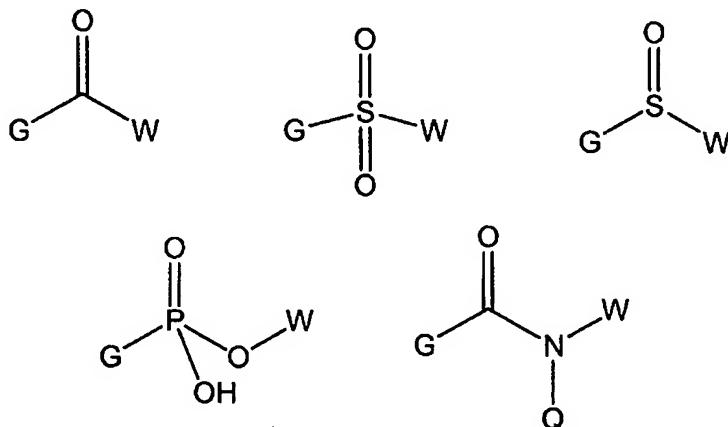
29. A method of solution phase combinatorial synthesis of compounds of  
20 claim 1, comprising the step of alkylating a free hydroxyl on a compound of formula IV or formula VI, wherein

R6 and R7 are hydrogen, or together form a carbonyl oxygen;

R1 is selected from the group consisting of hydrogen; -N(Z)Y and -C(Z)Y wherein;

When R1 is -N(Z)Y, then:

- 5 Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(Y)Z;



- 10 Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

- 15

The groups X1 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

- 20 When R1 is -C(Z)Y, then:

Y is selected from the group consisting of two hydrogen atoms, a double bonded oxygen (=O) to form a carbonyl, and a triple bonded nitrogen to form a nitrile,

Z is absent, or is selected from hydrogen or U,

Wherein U is selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aminoalkyl, aminoaryl, aryloxy, alkoxy, heteroaryloxy, aminoaryl, aminoheteroaryl, thioalkyl, thioaryl or thioheteroaryl, acyl, arylacyl, 5 heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

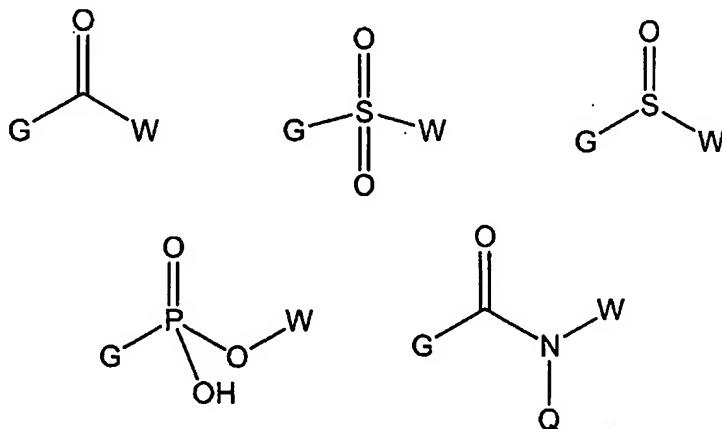
R5, R4, R3, and R2 are selected from the group consisting of OH, O-acyl, N<sub>3</sub>, NHDde, NHDTMP, NHZ, NHBOC, phthalimide, OX2, N(T)Y and an O-protecting group,

10 X2 is independently selected from alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl or heteroarylalkyl of 1 to 20 atoms,

T is hydrogen or X2,

Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(Y)Z;

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Z is selected from hydrogen or X1;

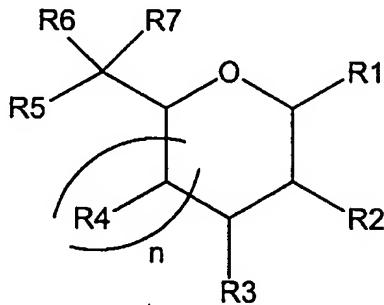
Q is selected from hydrogen or W;

20 The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

The groups X1 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

- 5 and any one of the protecting substituents may be removed prior to alkylation.

30. A compound of formula I



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formula I

Wherein,

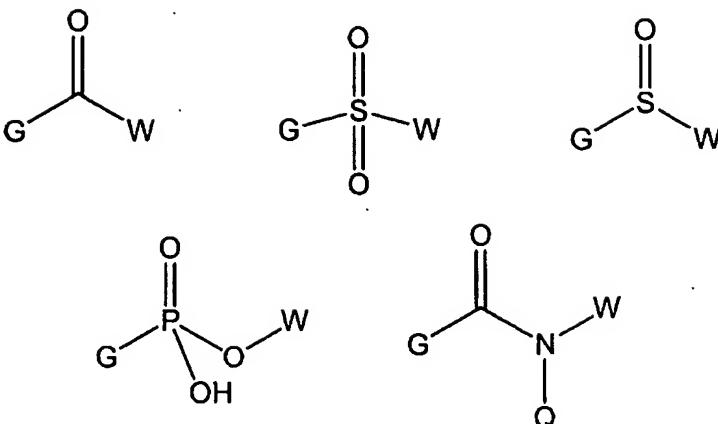
n is 0 or 1;

15 R6 and R7 are hydrogen, or together form a carbonyl oxygen;

R1 is selected from the group consisting of hydrogen; -N(Z)Y and -C(Z)Y wherein;

When R1 is -N(Z)Y, then:

20 Y is selected from hydrogen, or the following, where G denotes the point of connection to the nitrogen atom in N(Y)Z;



Z is selected from hydrogen or X1;

Q is selected from hydrogen or W;

5 The groups W are independently selected from the group consisting of alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

The groups X1 are independently selected from the group consisting  
10 of alkyl, alkenyl, alkynyl, heteroalkyl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

When R1 is  $-C(Z)Y$ , then:

15 Y is selected from the group consisting of two hydrogen atoms, a double bonded oxygen ( $=O$ ) to form a carbonyl, and a triple bonded nitrogen to form a nitrile,

Z is absent, or is selected from hydrogen or U,

Wherein U is selected from the group consisting of alkyl, alkenyl,  
20 alkynyl, heteroalkyl, aminoalkyl, aminoaryl, aryloxy, alkoxy, heteroaryloxy, aminoaryl, aminoheteroaryl, thioalkyl, thioaryl or thioheteroaryl, acyl, arylacyl, heteroarylacyl, aryl, heteroaryl, arylalkyl and heteroarylalkyl of 1 to 20 atoms,

- When R1 is H, at least two of the groups R2, R3, R4 and R5 are selected from the group consisting of  $-OX_2$  or  $-N(T)Y$ , and the others are independently selected from hydrogen,  $-OH$ ,  $-OX_2$ ,  $-N(T)Y$ , wherein Y is as defined above, T is selected from hydrogen or X2; and X2 is independently selected from alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl or heteroarylalkyl of 1 to 20 atoms,
- 5

- When R1 is  $N(Z)Y$  or  $C(Z)Y$ , at least one of the groups R2, R3, R4 and R5 are selected from the group consisting of  $-OX_2$  or  $-N(T)Y$ , and the others are independently selected from hydrogen,  $-OH$ ,  $-OX_2$ ,  $-N(T)Y$ , wherein Y is as defined above, T is selected from hydrogen or X2; and X2 is independently selected from alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, arylalkyl or heteroarylalkyl of 1 to 20 atoms,
- 10

- With the provisos that:
- 15     a X2 may not be another carbohydrate ring, a cyclitol ring or contain another carbohydrate ring,  
      b all of the X2 substituents may not be the same, and  
      c when R1 is  $C(Z)Y$ , and Z is C=O and R5 is  $N(T)Y$ , both T and Y may not be hydrogen, or Y may not be an amino acid or peptide.

20